Introduction to Organic Chemistry
Unit 1: Importance of Functional Groups

By the end of this unit you should be able to:

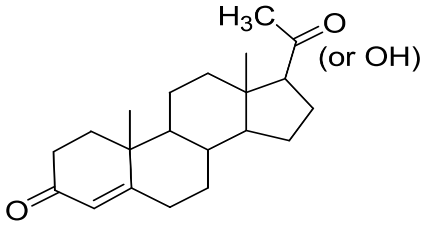
- convert a Lewis structure of an organic molecule to its condensed form and vice versa
- given a condensed form of a structure of an organic molecule determine its molecular formula, determine the hybridization of each atom in the molecule and identify the functional groups present in it
- by recognizing the functional groups label in a molecule all bonds as polar or non-polar and identify the various types of intermolecular forces (*van der Waals, dipole-dipole and hydrogen-bonding*) that are possible
- given a series of organic molecules of similar molecular weight predict their relative melting and/or boiling points

What is organic chemistry?

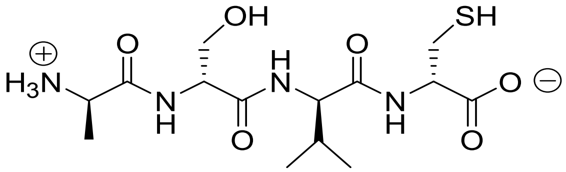
- By definition it is a branch of chemistry of compounds that contain the element carbon. While this seems like a very narrow group of compounds, of the more than 10 million known molecules over 80% are classified as organic molecules!

- Organic chemistry is ubiquitous- from the moment you woke up this morning you have constantly experienced aspects of organic chemistry in your life!
    - You likely eliminated organic molecules in your trip to the toilet
    - You used organic molecules in the shower to wash and shave, and brush your teeth. The smells in your after shave or perfumes are organic molecules.
    - Your breakfast included organic molecules like starch in your toast and cereal and your orange juice had vitamins, your coffee caffeine and sugar
    - Medications or vitamins you take are organic molecules
    - The clothes on your back, the shoes on your feet are made from organic molecules and dyes
    - The Gazette you're reading, television, your ipod ……need organic molecules
    - The car/ bus you took to campus has plastics, needs tires and fuels
    - You are a carbon based life form- DNA, proteins, peptides, neurotransmitters etc!

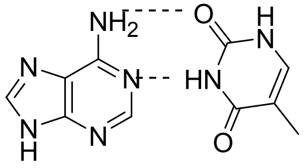
Examples of organic molecules in your life!



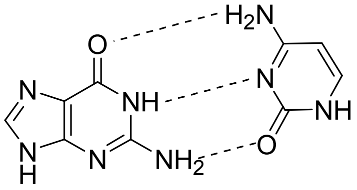
Progesterone/testosterone



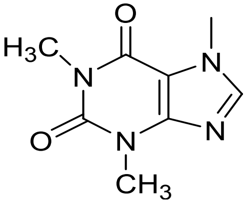
peptides



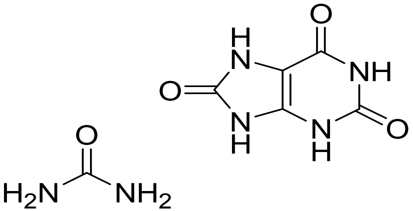
Adenine Thymine



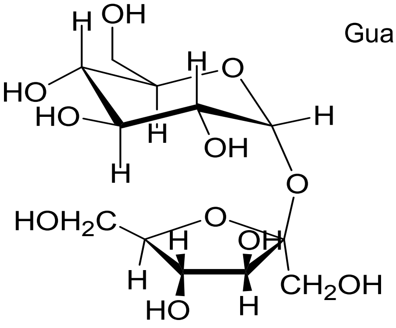
Guanine Cytosine



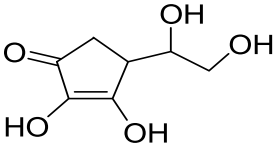
caffeine



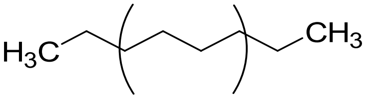
Urea and uric acid



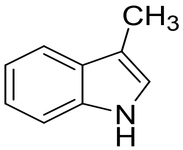
sucrose



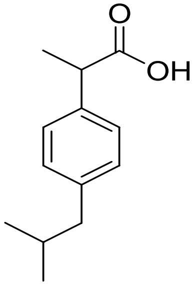
Vitamin C



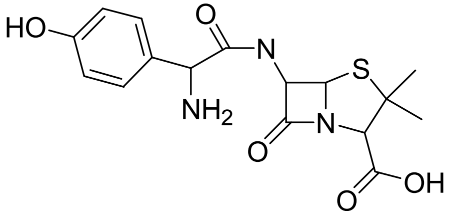
Hydrocarbons- fuels



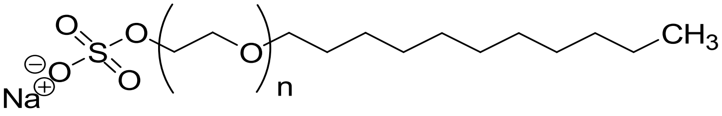
skatole



ibuprofen



amoxicillin

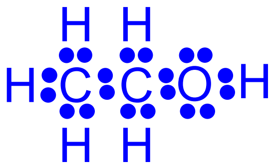


Lauryl ether sulfate

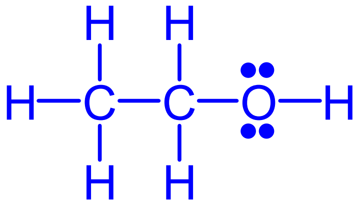
Structural Formulas

- Because many organic compounds contain many carbon and hydrogen atoms as well as other atoms, drawing full Lewis structures becomes too complicated and messy.
- Organic chemists use short-hand techniques to show (imply) the locations of electrons and bonds in molecules. The conventions are shown below for ethanol, molecular formula C_2H_6O.

Full Lewis dot structure
(all valence electrons shown)

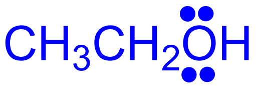


Lewis structure, with covalent bonds represented as lines.



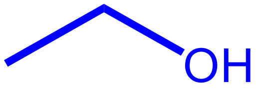
Covalent bonds omitted, but assumed. With or without non-bonding pairs. Used for simple molecules.

CH_3CH_2OH



$CH_3CH_2\ddot{\underset{\bullet\bullet}{O}}H$

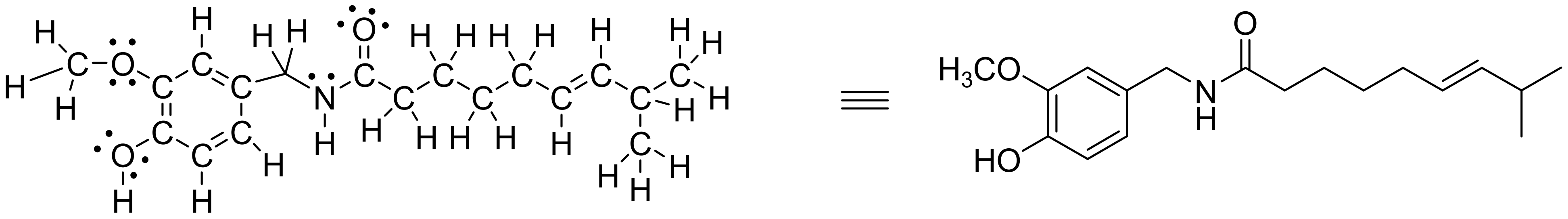
C-C bonds shown only by a line.
H atoms bonded to C not shown



These line diagrams *only show the bonding sequences* and are not designed or intended to show the actual 3D structure. Line diagrams are often used for larger molecules.

- Each solid line represents a two electron covalent bond
- When no atom is drawn at the intersection of two covalent bonds (two lines) it is assumed to be a carbon atom
- Hydrogen atoms bonded to carbons are not shown. Because carbon is always a valence of four, we assume that there are enough hydrogen atoms around each carbon as necessary to make it tetravalent
- All non-carbon atoms (heteroatoms) are drawn with the hydrogens bonded to them
- Lone pairs are often not drawn, and are assumed to be there

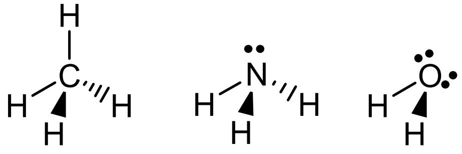
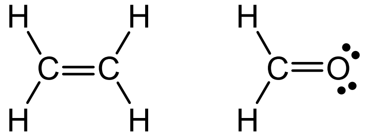
Eg. ***Capsaicin***- the molecule responsible for the spiciness of hot peppers



Practice: What are the molecular formula for capsaicin and the molecules shown on page 3?

Molecular Shapes

- The basic shapes of organic molecules are well-predicted by VSEPR theory discussed in the previous section.

Regions of e⁻ density around central atom	Predicted shape of electrons	Angles	Examples
4	tetrahedral	109.5° (and less)	
3	trigonal planar	120°	
2	linear	180°	$O=C=O$ $H-C\equiv C-H$

- Lone pairs of electrons exert a greater repulsive force than pairs in bonds, causing a reduction in bond angles.
- Double and triple bonds act as single region of electron density in VSEPR theory

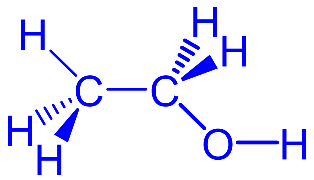
- By applying VSEPR shapes to all bonded sites in a molecule, the correct shape of nearly every organic molecule can be predicted and drawn in 3D
- The dot-line-wedge symbolism is the most common way of depicting three-dimensional structures:

Line: represents a bond
in the plane of the paper

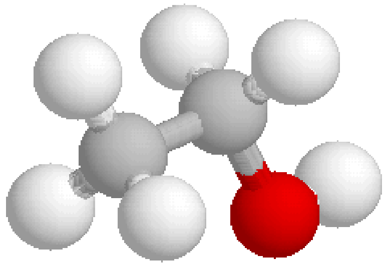
Dotted line: represents a bond directed
behind the plane of the paper

Wedged line: represents a bond directed
in *front of the plane* of the paper

- The 3D structure of ethanol is therefore represented as:



- The best 3D representation of ethanol is given by molecular models, or drawn as ball and stick models.
  - C = grey, H = white, O = red



We will see more of this latter in this type of representation later in this organic unit.

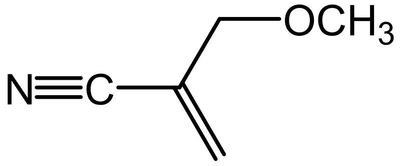
Hybridization

- Recall we discussed hybridization in the previous unit
- For organic molecules there are only three types of hybridization we need to worry about

Regions of e^- density	**Atomic orbitals**	**Hybrid orbitals**	**Electronic arrangement**
2	one *s*, one *p*	two *sp*	Linear
3	one *s*, two *p*	three sp^2	trigonal planar
4	one *s*, three *p*	four sp^3	tetrahedral

  - o *Regions of electron density*: an NB pair, a single bond, or a multiple bond each constitutes one region.
  - o *Electronic arrangement* may not equate to molecular shape if there is one or more NB pair present.

- Example: label the hybridization and give the approximate bond angles for C, N, and O in this molecule.



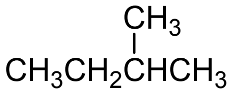
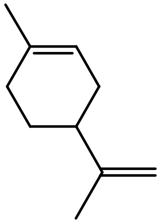
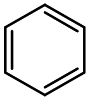
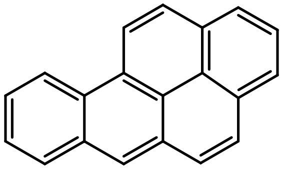
Functional Groups

- A **functional group** is an atom or a group of atoms within a molecule that have characteristic physical properties and are often the sites of chemical reactivity.

- A functional group determines all of the following properties of a molecule:
    - Bonding and shape
    - Type and strength of intermolecular forces
    - Physical properties
    - Chemical reactivity
    - Nomenclature

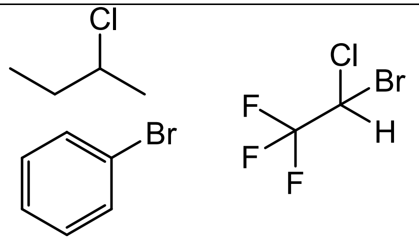
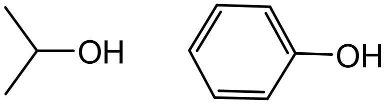
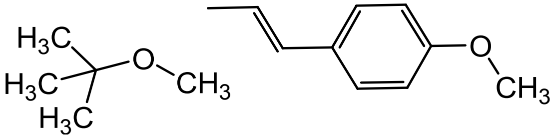
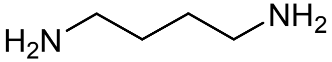
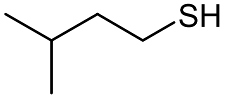
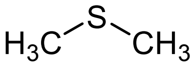
In Chem 20 we will introduce the first three and leave how they determine reactivity (and nomenclature) to second year organic chemistry.

Functional Groups: Hydrocarbons

Type of Compound	General structure	Functional Group	Hybridization	Example
alkane	$R_3C{-}H$ C_nH_{2n+2}	------	sp^3	 $CH_3CH_2\overset{\overset{CH_3}{\mid}}{C}HCH_3$
alkene	$R_2C{=}CR_2$ C_nH_{2n}	Double bond	$C{=}C$ sp^2	
alkyne	$RC{\equiv}CR$ C_nH_{2n-2}	Triple bond	$C{\equiv}C$ sp	$HC{\equiv}CCH(CH_3)_2$
aromatic compounds	contain 	Phenyl group	C-C sp^2	

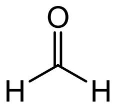
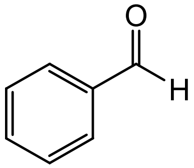
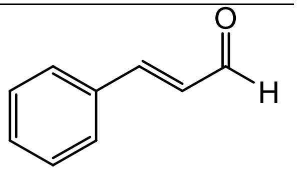
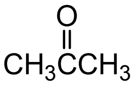
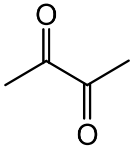
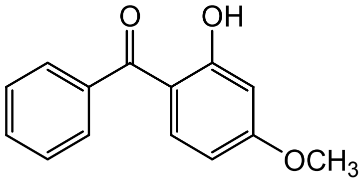
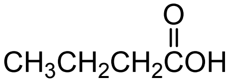
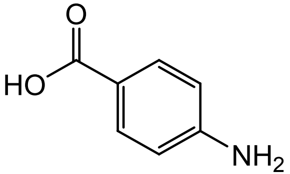
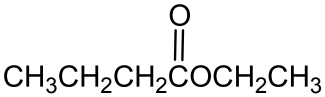
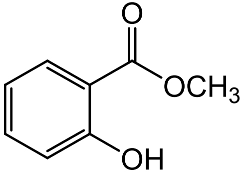
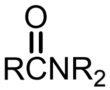
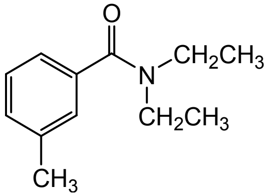
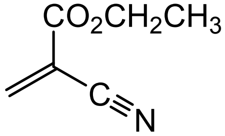
In all functional groups listed above, R = any chain of carbon atoms, or sometimes, an H atom, if H does not result in a different functional group.

Functional Groups: compounds containing a C-Z single bond

Type of Compound	General formula	Functional Group	Hybridization	Example
alkyl (aryl) halide	R-X (X = F, Cl, Br, I)	- X Halo group	Alkyl C-X sp^3 Aryl C sp^2;X = sp^3	
alcohol	R−OH	-OH hydroxy group	C sp^3 O sp^3	
ether	R−O−R	-OR Alkoxy group	C sp^3 O sp^3	
amine	R−NH$_2$ Or R$_2$NH Or R$_3$N	-NH$_2$ amino group	C sp^3 N sp^3	
thiol	R−SH	-SH Mercapto group	C sp^3 S sp^3	
sulphide	R-S-R	-SR alkylthiol	C sp^3 S sp^3	

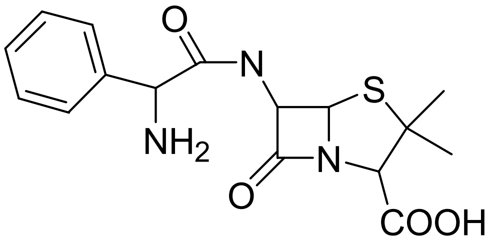
In all functional groups listed above, R = any chain of carbon atoms, phenyl or sometimes, an H atom, if H does not result in a different functional group.

Functional Groups: compounds containing a C=O Group

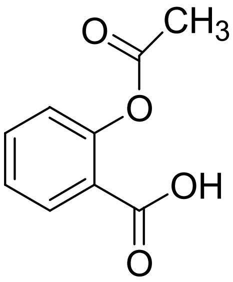
Type of compound	General formula	Functional group	Hybridization	Examples
aldehyde	 $R\overset{O}{\overset{\|}{C}}H$	C=O carbonyl	C sp^2 O sp^2	  
ketone	 $R\overset{O}{\overset{\|}{C}}R$	C=O carbonyl	C sp^2 O sp^2	 $CH_3\overset{O}{\overset{\|}{C}}CH_3$  
carboxylic acid	 $R\overset{O}{\overset{\|}{C}}OH$	-COOH carboxy	C sp^2 O sp^2	 $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OH$ 
ester	 $R\overset{O}{\overset{\|}{C}}OR$	-COOR	C sp^2 O sp^2	 $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$ 
amide	 $R\overset{O}{\overset{\|}{C}}NR_2$	$-CONH_2$ -CONHR $-CONR_2$	C sp^2 O sp^2 N sp^2	
nitrile	R-C≡N	R-C≡N	C sp N sp	

In all functional groups listed above, R = any chain of carbon atoms, or sometimes, an H atom, if H does not result in a different functional group.

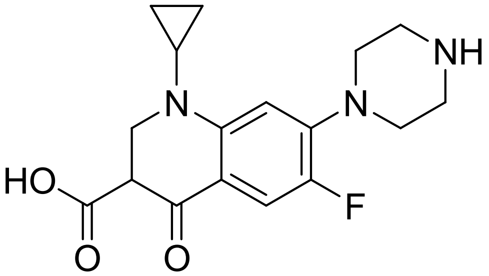
Practice: Identify the functional groups in the following molecules (you can also assign hybridization to each atom and determine their molecular formula)



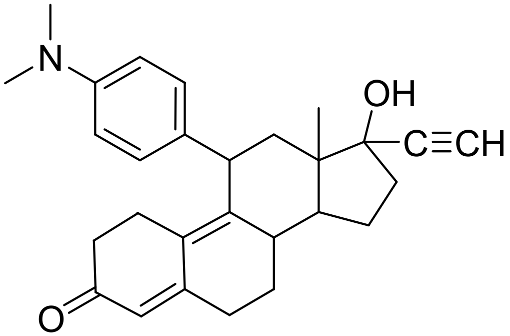
ampicillin



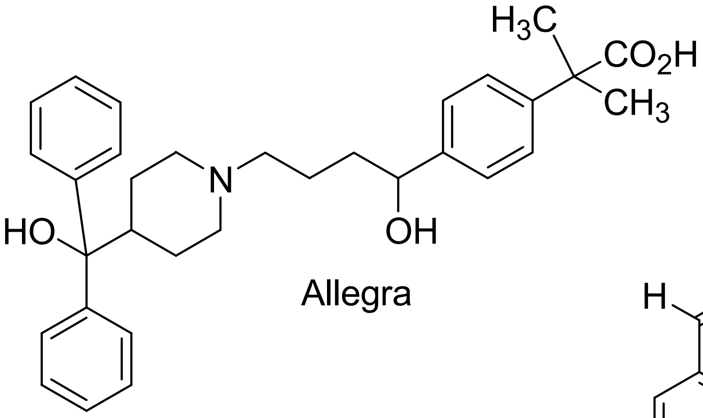
acetylsalicylic acid



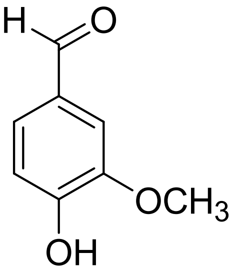
ciprofloxin



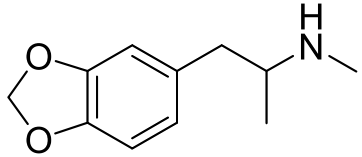
mifepristone



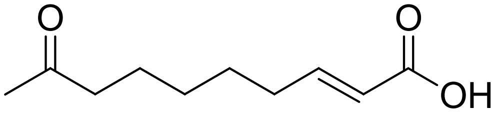
Allegra



vanillin



ectasy: methylenedioxymethampetamine

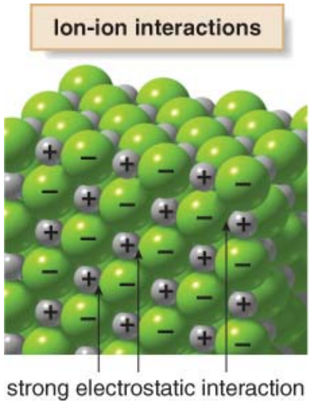


honey bee queen pheromone

Intermolecular Forces

- Intermolecular forces are also referred to as non-covalent interactions or non-bonded interactions, they are weaker interactions than ionic interactions.

- Ionic compounds contain oppositely charged particles held together by extremely strong electrostatic interactions. These ionic inter-actions are much stronger than the intermolecular forces present between covalent molecules.



- Covalent compounds are composed of discrete molecules. The nature of the forces between these molecules depends on the functional group(s) present.

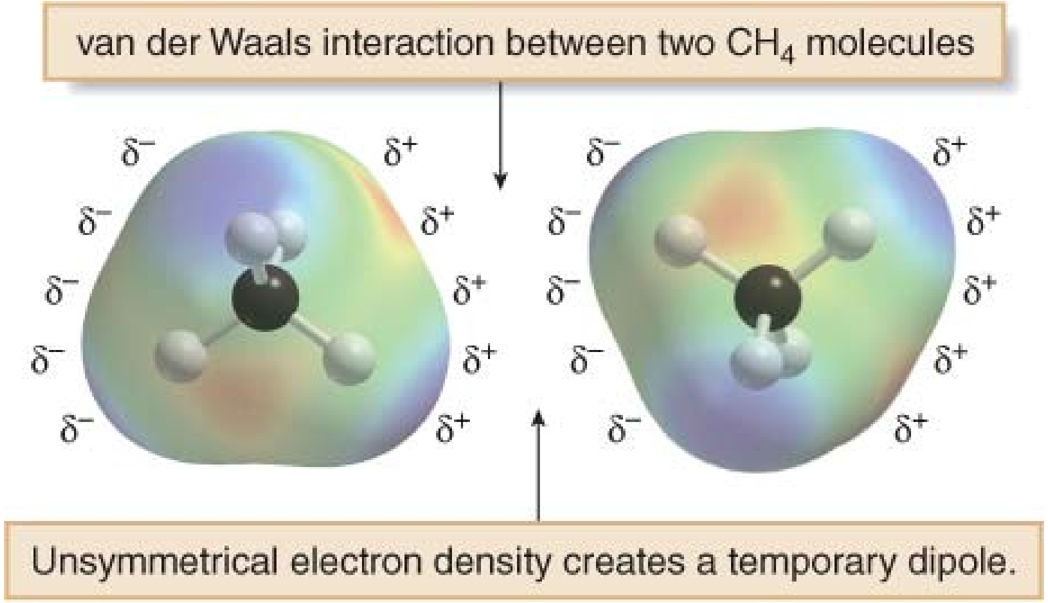
There are three different types of interactions, shown in order of increasing strength:

- **van der Waals forces**
- **dipole-dipole interactions**
- **hydrogen bonding**

Intermolecular Forces—van der Waals Forces

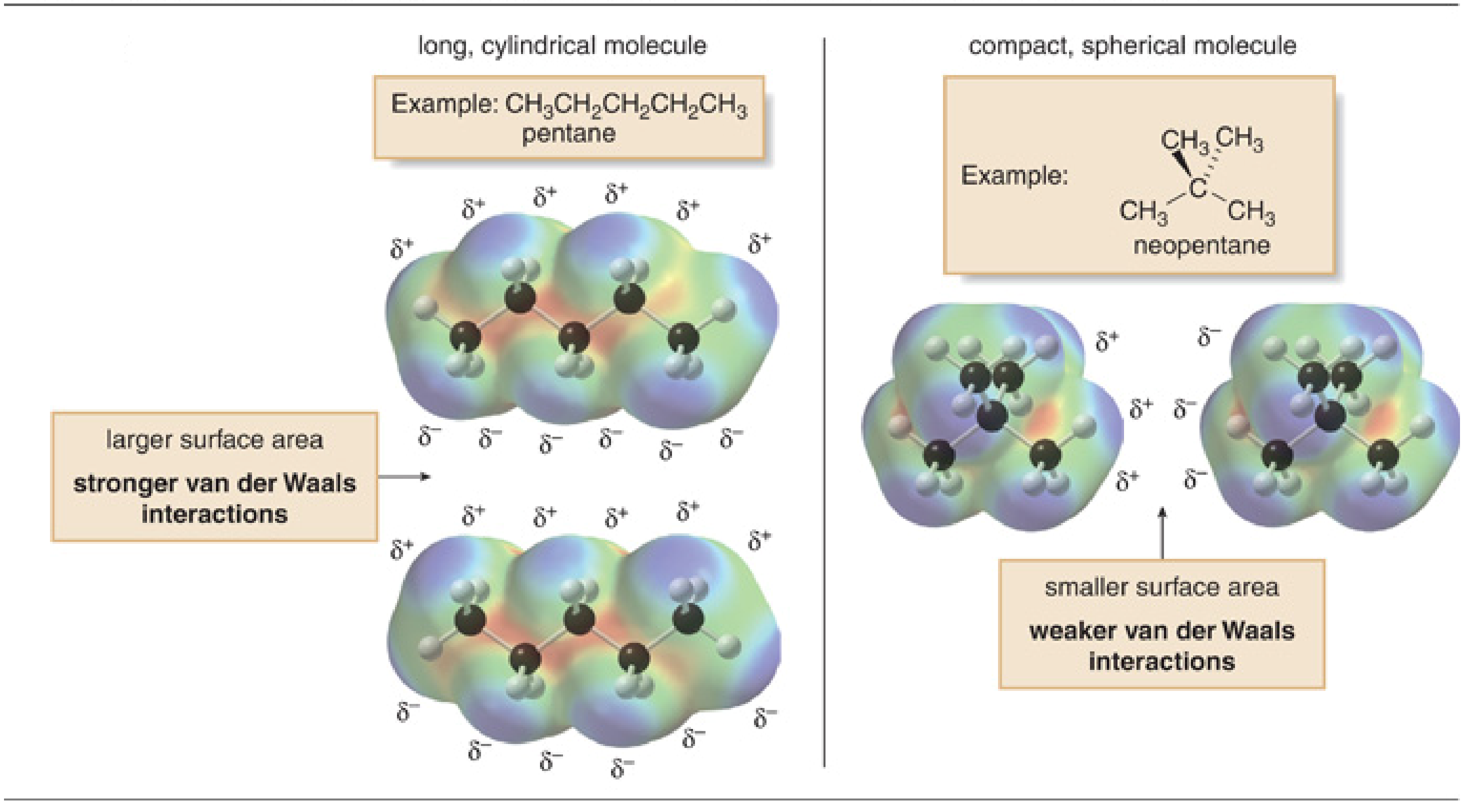
- van der Waals forces are also known as London forces.
- They are weak interactions caused by momentary changes in electron density in a molecule.
- They are the only attractive forces present in nonpolar compounds.
- All compounds exhibit van der Waals forces.

Eg. Even though CH_4 (or other alkane) has no net dipole, at any one instant its electron density may not be completely symmetrical, resulting in a temporary dipole. This can induce a temporary dipole in another molecule. The weak interaction of these temporary dipoles is a van der Waals force.


van der Waals interaction between two CH_4 molecules

Unsymmetrical electron density creates a temporary dipole.

- The surface area of a molecule determines the strength of the van der Waals interactions between molecules. The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces.

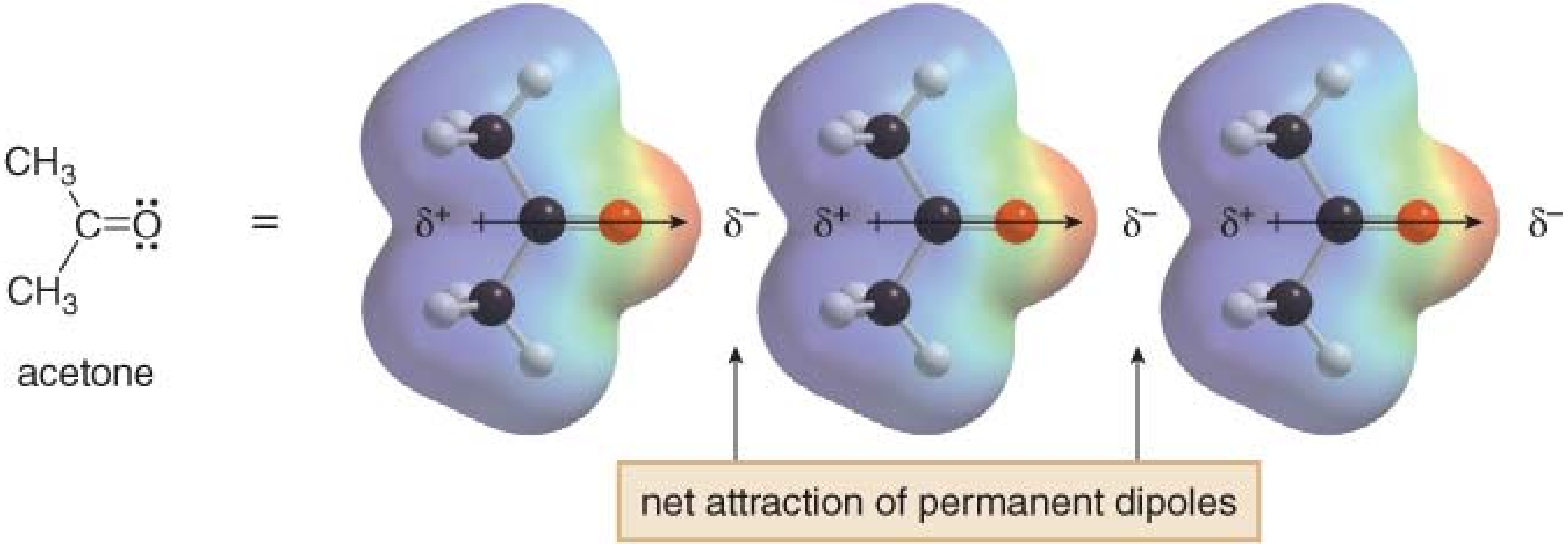


Intermolecular Forces—Dipole-Dipole Interactions

- Dipole—dipole interactions are the attractive forces **between the permanent dipoles** of two polar molecules.

- The *dipoles in adjacent molecules align so that the partial positive and partial negative charges are in close proximity*.

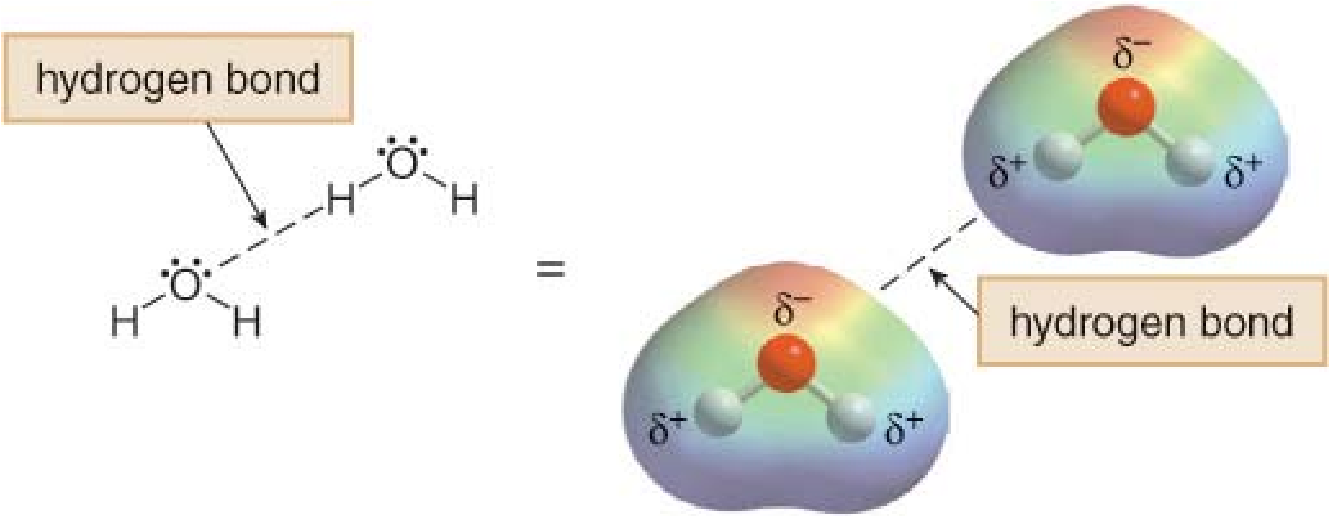
- These attractive forces caused by permanent dipoles are much stronger than weak van der Waals forces.



net attraction of permanent dipoles

Intermolecular Forces—Hydrogen-Bonding Interactions

- Hydrogen bonding typically occurs when a hydrogen atom bonded to O, N, or F, is electrostatically attracted to a lone pair of electrons on an O, N, or F atom in another molecule.



Summary of Types of Intermolecular Forces

Type of Force	Relative Strength	Exhibited by	*Examples*
Van der Waals	weak	All molecules	$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2CH_2OH$ $CH_3CH_2CH_2CH_2COOH$
dipole-dipole	moderate	Molecules with a net dipole	$CH_3CH_2CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2CH_2OH$ $CH_3CH_2CH_2CH_2COOH$
hydrogen-bonding	strong	Molecules with N-H, O-H or H-F bonds	$CH_3CH_2CH_2CH_2CH_2OH$ $CH_3CH_2CH_2CH_2COOH$
ion-ion	very strong	Ionic compounds	$CH_3CH_2CH_2CH_2COO$- Na+ NaCl

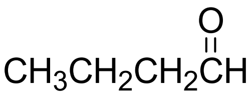
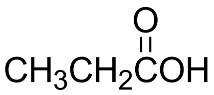
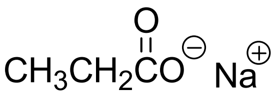
Physical Properties- Boiling points and Melting Points

- The stronger the intermolecular forces, the higher the boiling point/melting point.
- Because ionic compounds are held together by extremely strong interactions, they have very high melting points.
- For compounds with approximately the same molecular weight:

compounds with van der Waals interactionc → **compounds with dipole-dipole interactions** → **compounds with Hydrogen Bonding interactionc** → **compounds with ionic interactions**

increased strenth of intermolecular forces
Increasing boiling point

Eg.

$CH_3CH_2CH_2CH_2CH_3$	 $CH_3CH_2CH_2\overset{O}{\overset{\|\|}{C}}H$	$CH_3CH_2CH_2CH_2OH$	 $CH_3CH_2\overset{O}{\overset{\|\|}{C}}OH$	 $CH_3CH_2\overset{O}{\overset{\|\|}{C}}O^{\ominus}\ Na^{\oplus}$
bp = 36 °C	bp = 75 °C	bp = 116 °C	bp = 141 °C	mp = 289°C
mp = -130 °C	mp = -96 °C	mp = -90 °C	mp = -21 °C	

increased strenth of intermolecular forces
Increasing boiling point

For two compounds with similar functional groups:

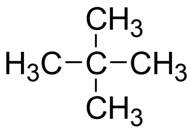
- The larger the surface area, the higher the melting and boiling point.

$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_2CH_3$
bp = 0 °C	bp = 36 °C	bp = 69 °C
mp = -138 °C	mp = -129 °C	mp = -95 °C

increased surfeace area
increasing boiling and melting point

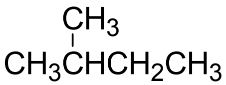
- The boiling point of isomers (same molecular formula, different structure) decreases with branching because of decreasing surface area

increased branching
decrease surface area



$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ CH_3 \end{array}$$

bp = 10 °C



$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$$

bp = 30 °C

$CH_3CH_2CH_2CH_2CH_3$

bp = 36 °C

increased surfeace area
increasing boiling point

- Symmetry plays a role in determining the melting points of compounds having the same functional group and similar molecular weights, but very different shapes.

- A compact symmetrical molecule like neopentane packs well into a crystalline lattice whereas isopentane, which has a CH_3 group dangling from a four-carbon chain, does not. Thus, neopentane has a much higher melting point.